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Photoluminescent epoxy microspheres: preparation, surface functionalization *via* grafting polymerization and photophysical properties

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In this contribution, we reported the preparation of photoluminescent epoxy microspheres. First, diglycidyl ether of tetraphenylethene (DGETPE), a novel epoxy monomer bearing tetraphenylethene was synthesized and then it was incorporated into a commercial epoxy (*viz.* diglycidyl ether of bisphenol A) to obtain the epoxy microspheres with sizes of 1–3 μm *via* a phase-inverted reaction-induced phase separation approach. It was found that the epoxy microspheres were luminescent under UV light radiation. The surfaces of the photoluminescent epoxy microspheres were further functionalized with poly(*N*-vinyl pyrrolidone) (PVPy) with a grafting-from methodology *via* reversible addition–fragmentation chain transfer/macromolecular design *via* the interchange of xanthate (RAFT/MADIX) process. The PVPy-grafted epoxy microspheres can be well dispersed into aqueous solutions. The morphologies and photophysical properties of the epoxy microspheres were investigated by means of scanning electron microscopy, and UV-vis and fluorescence spectroscopy.

Introduction

For most organic aromatic compounds, fluorescence intensity would be weakened upon increasing the concentration of their solutions. Such a concentration-quenching effect is attributable to the formation of sandwich-shaped excimers and exciplexes aided by the collisional interactions between the aromatic molecules in the excited and ground states.[1–3] In marked contrast to this common knowledge, nonetheless, Tang *et al.*[4–7] recently reported a class of novel molecules, the aggregation of which can induce and even intensify the emission of fluorescence. For instance, silole molecules and their derivatives are generally non-luminescent in the solution state but they became emissive in the aggregation state.[4,5] This novel phenomenon has been named as "aggregation-induced emission" (AIE) effect.[4,5] In the past years, many compounds such as tetraphenylethene (TPE),[4,6,8–11] benzobis(thiadiazole)[12,13] and 1,4-di[(*E*)-styryl]benzene[14] have been found (or/and synthesized), which can display such AIE effect. These compounds are potential to find a variety of applications in OLEDs, chemosensors and bioprobes[15–24] because the luminescent properties *via* AIE effect are exhibited in the aggregation state, which is in marked contrast to those luminogens to possess concentration-quenching effect. The mechanistic investigation shows that restriction of intramolecular rotation (RIR) in the aggregates is the main cause of the AIE effect. It is proposed that in solution, the multiple aryl rings of the AIE molecules can rotate around the single-bond axles linking the peripheral aryl rotor and the central stator. The free intramolecular rotation would convert photonic energy into heat and deactivates the excited states no-radioactively, thus making the molecules non-emissive. In the aggregates, however, the intramolecular free rotation is restricted and the non-radiative relaxation channel is obstructed and thus the molecules become emissive. The mechanism that restriction of intramolecular rotation (RIR) of multiple aryl groups in the above molecules is responsible for the AIE effect inspires one of designing other constraints to suppress intramolecular rotation to make these compounds emissive.

Epoxy microspheres are a class of important materials owing to their excellent thermal, dimensional stability and chemical resistance; they have been applied as coatings, adhesives, molding compounds, chromatographic column packing and substrates for medical diagnostics.[25–29] Generally, epoxy microspheres are prepared *via* dispersion polymerization[30,31] in the blends of epoxy with a liquid polyether (*e.g.*, polypropylene glycol, PPG). In this case, epoxy microspheres are formed and phase-separated out as the curing reaction proceeds.[32–38] The driving forces for the reaction-induced phase separation are: (i) the increased molecular weight owing to polymerization (*viz.* curing reaction), which gives rise to the decreased contribution of mixing entropy (ΔS_m) to the free energy of mixing (ΔG_m) and (ii) the alteration of the inter-component interaction parameters (χ) with conversion of monomers. The use of the liquid polyether is to facilitate the isolation of the resulting epoxy microspheres from the mixtures. In this approach, nonetheless, epoxy microspheres are the minor component whereas the

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liquid polyether is the major component. Recently, it was realized that epoxy microspheres can be alternatively prepared *via* so-called phase-inverted reaction-induced phase separation (PIRIPS) approach while thermoplastics are used instead of liquid polyethers. It is noted that phase inversion occurs at the low concentration of thermoplastics (*e.g.*, <20%). In marked contrast to dispersion polymerization approach, epoxy is a major component whereas thermoplastic polymers are the minor component in this approach. For instance, Woo *et al.*[39] have reported the preparation of epoxy microspheres in the thermosetting blends of epoxy with poly(methyl methacrylate) (PMMA). In the thermosetting blends containing up to 30 wt% of PMMA, dispersed epoxy microdomains were formed with the diameter of 10–80 μm after continuous PMMA matrices were removed *via* extraction with dichloromethane. Recently, Zheng *et al.*[40] reported that the preparation of epoxy microspheres with the size of 5–10 μm in diameter with the blends of epoxy with poly(ε-caprolactone) with PIRIPS approach. The PIRIPS behavior has been interpreted on the basis of spinodal decomposition mechanism,[32,34] which is involved with several competitive kinetics such as curing reaction, phase separation and changes of visco-elastomeric properties of component polymers. Compared to dispersion polymerization, the efficiency of preparation is significantly enhanced with PIRIPS approach.

Generally, epoxy microspheres are not luminescent. It is of interest to prepare novel epoxy microspheres with photoluminescent properties. It is expected that photoluminescent epoxy microspheres could find more applications such as ink filler for currency anti-counterfeiting, luminescent coating and bioprobes. In addition, luminescent epoxy microspheres dispersed in water could be used for the detection of wastewater on the basis of fluorescent quenching.[41] To the best of our knowledge, there has been no previous report on the preparation of photoluminescent epoxy microspheres. In this work, we explored to prepare luminescent epoxy microspheres *via* PIRIPS approach. First, we synthesized diglycidyl ether of tetraphenylethene (DGETPE), a novel epoxy monomer bearing tetraphenylethene (TPE). Thereafter, DGETPE together with diglycidyl ether of bisphenol A (DGEBA) was used to obtain the luminescent epoxy microspheres with the thermosetting blends of epoxy with poly(ε-caprolactone) *via* PIRIPS approach. It has been known that tetraphenylethene (TPE) and its derivatives are capable of displaying AIE effect.[4,6,9–11] It is expected that the incorporation of TPE structural units into epoxy thermosets could achieve the restriction of intramolecular rotation (RIR) of TPE *via* the formation of crosslinking networks (*viz.*, vitrification of polymer), making the moieties emissive. This strategy is in marked contrast to the case that RIR was fulfilled *via* the aggregation of TPE moieties.[4,6,9–11] The purpose of this work is to demonstrate this situation. To investigate the photophysical behavior of the epoxy microspheres in water, we further functionalized the surfaces of the luminescent epoxy microspheres with poly(*N*-vinyl pyrrolidone) (PVPy), a water-soluble polymer with a grafting-from methodology *via* reversible addition–fragmentation chain transfer/macromolecular design *via* the interchange of xanthate (RAFT/MADIX) process. In this work, the morphologies of the epoxy microspheres were characterized by means of scanning electron microscopy (SEM), UV-vis and fluorescence spectroscopy.

Experimental

Materials

p-Methoxybenzophenone was purchased from TCI Co., Shanghai, China. Titanium(IV) chloride ($TiCl_4$), zinc powder, boron tribromide and 2-bromopropionyl bromide were purchased from Aldrich Co., Shanghai, China. Epichlorohydrin, sodium hydroxide (NaOH), sodium bicarbonate ($NaHCO_3$), magnesium sulfate ($MgSO_4$), 4,4-diaminodiphenylsulfone (DDS) were obtained from Shanghai Reagent Co., China. Diglycidyl ether of bisphenol A (DGEBA) was supplied from Shanghai Resin Co., China and it has a quoted epoxide equivalent weight of 185–210. Poly(ε-caprolactone) (PCL) was purchased from Aldrich Co., USA and it had a quoted molecular weight of $M_n = 50\ 000$ Da. 2,2-Azobisisobutylnitrile (AIBN) was purchased from Shanghai Reagent Co., China and was recrystallized from acetone twice before use. *N*-Vinyl-2-pyrrolidinone (NVP) was purchased from Aldrich Co., Shanghai, China and it was purified by passing alkaline aluminum oxide column to remove the inhibitor. Potassium ethyl xanthate was synthesized by following the method of literature.[42] The organic solvents such as tetrahydrofuran (THF) and triethylamine (TEA) were obtained from commercial source. Before use, THF was refluxed over metal sodium and then distilled; trimethylamine was refluxed with *p*-toluenesulfonyl chloride and then distilled. Dichloromethane (DCM) was dried over CaH_2 and then distilled. All other reagents and solvents used in this work were purchased from Shanghai Reagent Co., China.

Synthesis of dimethoxytetraphenylethylene (DMOTPE)

Dimethoxytetraphenylethylene (DMOTPE) was synthesized with McMurry coupling reaction.[43,44] Typically, to a flask equipped with a magnetic stirrer, zinc powder (6.540 g, 100.0 mmol) and THF (80 mL) were charged under an argon atmosphere with vigorous stirring. This mixture was cooled to 0 °C, and then titanium(IV) chloride ($TiCl_4$) (2.200 mL, 20.0 mmol) was dropwise added. The system was refluxed for 3 hours and cooled to 0 °C and then *p*-methoxybenzophenone (2.120 g, 10.0 mmol) dissolved in THF (60 mL) was dropwise added into the system. The mixture was refluxed overnight. After reaction, the system was cooled down to room temperature and the reaction was quenched by adding the saturated aqueous solution of sodium bicarbonate ($NaHCO_3$) until no bubbles were released. The reacted mixture was then filtered and the filtrate was extracted with dichloromethane (DCM). The organic layer was dried with anhydrous magnesium sulfate ($MgSO_4$) overnight and then filtered. With rotary evaporation, the crude product was obtained. The crude product was purified by recrystallization from the mixture of dichloromethane with methanol (2 : 1 vol) and the product (1.629 g) was obtained with the yield of 83%. ^1H NMR ($CDCl_3$, ppm): 7.10–7.05 (*m*, 10H, $-C_6\boldsymbol{H}_5$), 6.92 (*d*, 4H, *m*-$C_6\boldsymbol{H}_2$, *J* = 8.8 Hz), 6.63 (*d*, 4H, *o*-$C_6\boldsymbol{H}_2$, *J* = 8.8 Hz) and 3.73 (*m*, 6H, –$OC\boldsymbol{H}_3$).

Synthesis of dihydroxytetraphenylethylene (DHTPE)

To a flask equipped with a magnetic stirrer, DMOTPE (2.000 g, 5.1 mmol) and DCM (30 mL) were charged with vigorous stirring. The system was cooled to −78 °C and then boron tribromide (5.110 g, 20.4 mmol) dissolved in 20 mL of DCM was added with vigorous stirring for 15 min. After the system was warmed to room temperature, the reaction was performed for additional 12 hours. The flask was then immersed into an ice-water bath and then deionized water (40 mL) was dropwise added with vigorous stirring. The hydrolysis reaction was carried out at room temperature with vigorous stirring for one hour. The organic layer was isolated and washed with deionized water three times. After dried with anhydrous $MgSO_4$, the solvent was eliminated *via* rotary evaporation. The crude product was further purified with recrystallization from the mixture of acetone with water (9 : 1 vol) and the product (1.634 g) was obtained with the yield of 88%. ^1H NMR ($CDCl_3$, ppm): 7.13–7.01 (*m*, 10H, –$C_6\boldsymbol{H}_5$), 6.90 (*d*, 4H, *m*-$C_6\boldsymbol{H}_2$, *J* = 9.2, 13.6 Hz), 6.59 (*d*, 4H, *o*-$C_6\boldsymbol{H}_2$, *J* = 8.4, 12.0 Hz) and 4.64 (*s*, 2H, –O***H***).

Synthesis of diglycidyl ether of tetraphenylethene (DGETPE)

To a flask equipped with a mechanical stirrer, a constant pressure dropping funnel and a graham condenser, DHTPE (1.000 g, 2.74 mmol) and epichlorohydrin (2.530 g, 27.4 mmol) were charged with vigorous stirring and then the saturated solution of NaOH (2.5 mL) was slowly added. The mixture was refluxed for 2 hours. Cooled to room temperature, the reacted mixture was diluted with DCM (50 mL) and washed with the saturated aqueous solution of NaCl (20 mL) and deionized water (20 mL) to neutrality. The organic layer was dried with anhydrous magnesium sulfate and filtered. With rotary evaporation, the crude product was obtained. The crude product was purified by passing a silica gel column with the mixture of hexane with ethyl acetate (4 : 1 vol) as the eluent. With rotary evaporation, the product (1.072 g) was obtained with the yield of 82%. ^1H NMR ($CDCl_3$, ppm): 7.01–6.96 (*m*, 10H, –$C_6\boldsymbol{H}_5$), 6.82 (*d*, 4H, *m*-$C_6\boldsymbol{H}_2$, *J* = 10.4 Hz), 6.57 (*d*, 4H, *o*-$C_6\boldsymbol{H}_2$, *J* = 8.4 Hz), 4.03 (*s*, 2H, –$C\boldsymbol{H}_2C_2H_3O$ of *trans*-DGEDPE), 3.80 (*s*, 2H, –$C\boldsymbol{H}_2C_2H_3O$ of *cis*-DGEDPE), 3.22 (*s*, 2H, –C***H***– of epoxide group), 2.79 (*s*, 2H, 2–$C\boldsymbol{H}_2$– of epoxide group of *trans*-DGETPE), 2.64 (*s*, 2H, –$C\boldsymbol{H}_2$– of epoxide group of *cis*-DGETPE).

Preparation of epoxy microspheres

DGEBA (2.700 g), PCL (1.730 g) and DGETPE (0.300 g) were mixed at 120 °C with continuous stirring until PCL was totally dissolved, and then DDS (1.050 g) was added with continuous stirring until the systems became homogeneous. The mixtures were cured at 150 °C for 3 hours and 180 °C for one hour to attain a complete curing reaction. The thermosetting blend of epoxy with PCL was ground and added to a beaker and 200 mL of THF was added with vigorous stirring until all of the pellets were dispersed in THF. The mixture was centrifuged to afford the solids. The solids were washed with THF three times to remove PCL. After drying in a vacuum oven at 30 °C for 24 hours, the epoxy microspheres were obtained.

Surface grafting polymerization of epoxy microspheres

First, the surfaces of the epoxy microspheres were functionalized with 2-bromopropionyl groups. To a flask equipped with a magnetic stirrer, the epoxy microspheres (1.500 g), THF (20 mL), and triethylamine (5 mL) were charged with vigorous stirring. To promote the dispersion of the epoxy microspheres, the mixture was subjected to ultrasonic irradiation for 20 min. Thereafter, 2-bromopropionyl bromide (8.240 g, 38.2 mmol) was dropwise added at 0 °C with vigorous stirring. The reaction was carried out at room temperature for 24 hours and the microspheres were isolated with a centrifuge. After washing with THF three times and dried *in vacuo* at 30 °C for 24 hours, the 2-bromopropionyl-functionalized epoxy microspheres were obtained. The content of bromine was measured to be 11.2 wt% by means of elemental analysis.

Second, the surfaces of the above 2-bromopropionyl-functionalized epoxy microspheres were subjected to the reaction with potassium ethyl xanthate to obtain the xanthate-functionalized epoxy microspheres. Typically, to a flask equipped with a magnetic stirrer, the above 2-bromopropionyl-functionalized epoxy microspheres (1.000 g) and acetone (10 mL) were charged. With ultrasonic irradiation for 30 min, potassium ethyl xanthate (0.700 g) was added. The reaction was carried out at room temperature for 24 hours and then the reacted epoxy microspheres were isolated with centrifuge. The as-obtained solids were then washed with THF three times. After drying *in vacuo* at 30 °C for 24 hours, the product was obtained.

Third, the surface grafting polymerization of *N*-vinyl pyrrolidone (NVP) was carried out with the above ethyl xanthate-functionalized epoxy microspheres as the chain transfer agent *via* a RAFT/MADIX process. To a flask equipped with a magnetic stirrer, the above xanthate-functionalized epoxy microspheres (0.200 g), NVP (0.600 g, 5.400 mmol), 1,4-dioxane (5 mL) and AIBN (8 mg, 0.049 mmol) were charged with vigorous stirring. The flask was connected onto a Schlenk line to degas *via* three freeze–pump–thaw cycles. The polymerization was performed at 70 °C for 24 hours, and the reacted epoxy microspheres were isolated *via* centrifuge. The as-obtained solids were then washed with the mixture of tetrahydrofuran with water (3 : 1 vol) three times. After drying in a vacuum oven at 30 °C for 24 hours, the product, PVPy-grafted epoxy microspheres were obtained by controlling the conversion of NVP to be *ca.* 11.5%.

Measurement and characterization

Nuclear magnetic resonance (NMR) spectroscopy. The NMR measurements were carried out on a Varian Mercury Plus 400 MHz NMR spectrometer at 25 °C. The samples were dissolved in deuterium chloroform and the solutions were measured with tetramethylsilane (TMS) as an external reference.

Fourier transform infrared (FTIR) spectroscopy. FTIR measurements were performed on a Perkin-Elmer Paragon 1000

FTIR spectrometer. The samples were granulated, and the powders were mixed with KBr and then pressed into small flakes for FTIR measurement. Before the measurements, the specimens were dried *in vacuo* at 60 °C for 48 hours. All of the specimens used in the study were sufficiently thin to be within a range where the Beer–Lambert law was obeyed. The spectra were obtained at a resolution of 2 cm^{-1} and are reported as the averages of 64 scans.

Scanning electron microscopy (SEM). The specimens were examined with a JEOL JSM 7401 F FESEM scanning electron microscope (SEM) at an activation voltage of 5 kV. Before the morphological observation, the surfaces of epoxy microspheres were coated with thin layers of gold of about 100 Å.

Elemental analysis. The content of bromine element was determined by means of a technique of oxygen flask combustion followed by titration with mercuric nitrate. The samples were first combusted in a 1.0 L oxygen-filled combustion flask containing 0.01 M nitric acid. After combustion, the flask was cooled, and the solution was titrated with a dilute standard silver nitrate solution to calculate the content of bromine. The value of bromine content was taken as the average of three measurements with a deviation of 5%. The contents of sulfur were determined by means of a technique of oxygen flask combustion. Samples were first catalytic oxidized in the high-temperature oxygen-rich environment. Gas mixture were separated effectively by a special adsorption–desorption device, and sulfur dioxide was collected to calculate the content of sulfur. The value of sulfur content was taken as the average of three measurements with a deviation of 5%.

Thermogravimetric analysis (TGA). A TA Instruments thermogravimetric analyzer (Q-5000) was used to investigate the thermal stability of the samples. The samples were heated in a nitrogen atmosphere from ambient temperature to 800 °C at a heating rate of 20 °C min^{-1} in all cases.

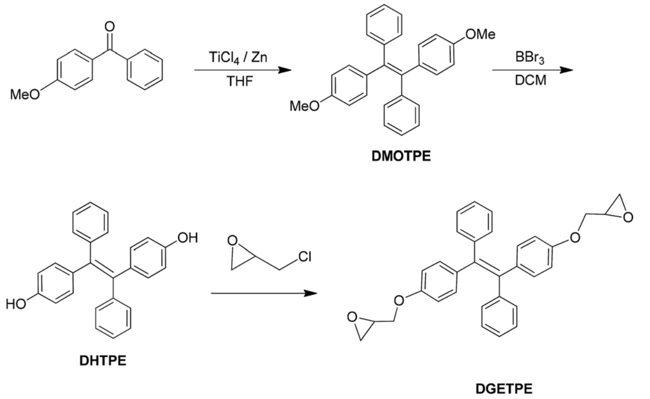
Ultraviolet-visible (UV-vis) spectroscopy. UV-vis spectroscopy was carried out on a Cary 60 spectrometer, Agilent Technologies, USA. The concentration of DGETPE in THF solution or the mixed solution of THF with water (THF : water = 1 : 99 vol) was set as 10.0 mM. The concentration of PVPy-grafted epoxy microspheres in the suspensions of water were set as 0.01, 0.03, 0.10, 0.33, 0.50 and 1.00 g L^{-1}, respectively.

Fluorescent (FL) spectroscopy. Fluorescent (FL) spectroscopy was carried out on a Perkin-Elmer LS 55 spectrometer. The FL spectra were obtained with a 450 W Xe lamp as a continuous UV light source at the wavelength of λ = 330 nm. Fluorescence quantum yield was measured with anthracene as the standard sample with its ethanol solutions.[45]

Results and discussion

Synthesis of DGETPE

The route of synthesis for diglycidyl ether of tetraphenylethene (DGETPE) is shown in Scheme 1. First, dimethoxytetraphenylethylene (DMOTPE) was synthesized *via* McMurry coupling reaction[43,44] of *p*-methoxybenzophenone in the presence of titanium(IV) chloride and metal zinc. Second, the demethylation reaction of DMOTPE was carried out to afford dihydroxytetraphenylethylene (DHTPE) by the use of baron tribromide (BBr_3), followed by treatment with water. Finally, the condensation between DMOTPE and epichlorohydrin was performed to afford diglycidyl ether of tetraphenylethene (DGETPE). Shown in Fig. 1 are the ^1H NMR spectra of DMOTPE, DHTPE and DGETPE. For DMOTPE, the signal of resonance at 3.73 ppm is assignable to the protons of methoxyl groups whereas the peaks in the range of 6.5–7.5 ppm are attributable to the protons of phenyl groups. Upon reacting with BBr_3, the



Scheme 1 Synthesis of diglycidyl ether of tetraphenylethene (DGETPE).

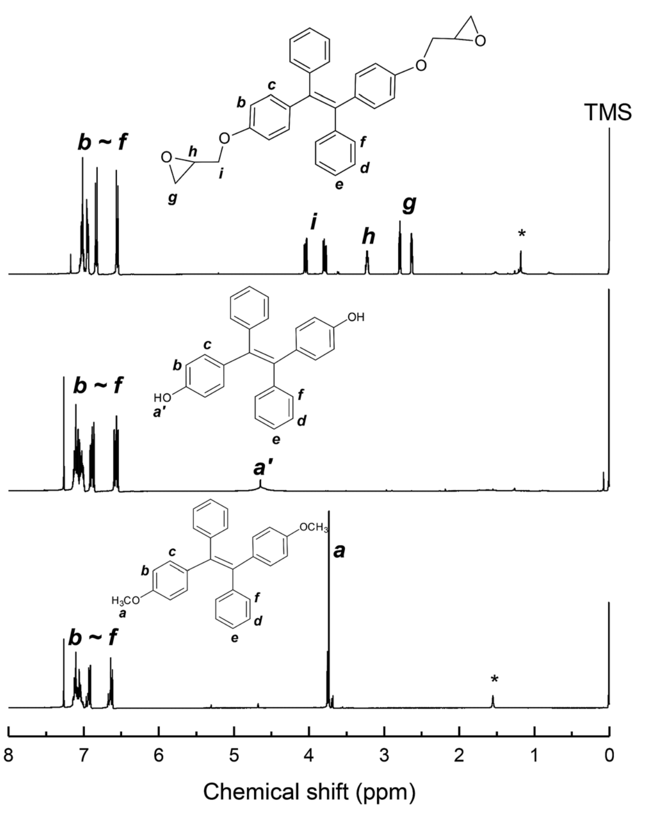


Fig. 1 ^1H NMR spectra of: DMOTPE (down), DHTPE (middle) and DGETPE (up). The signals of resonance labeled with asterisks (*) resulted from a trace of water in the deuterated solvent.

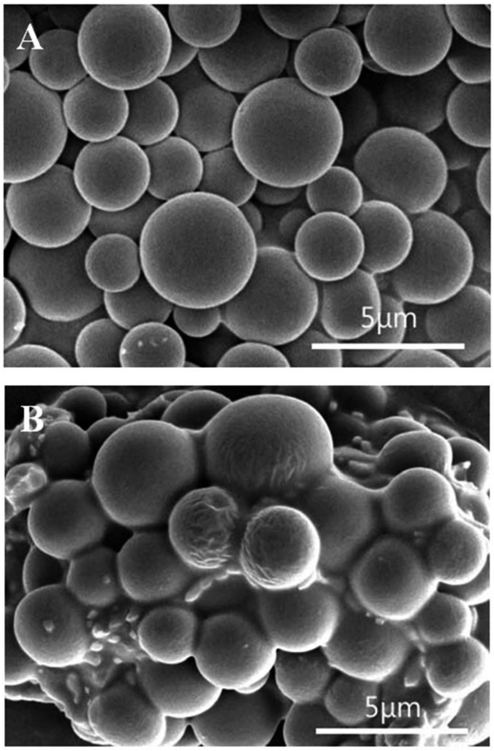


Fig. 2 SEM micrographs of luminescent epoxy microspheres: (A) unmodified epoxy microspheres, (B) PVPy-grafted epoxy microspheres.

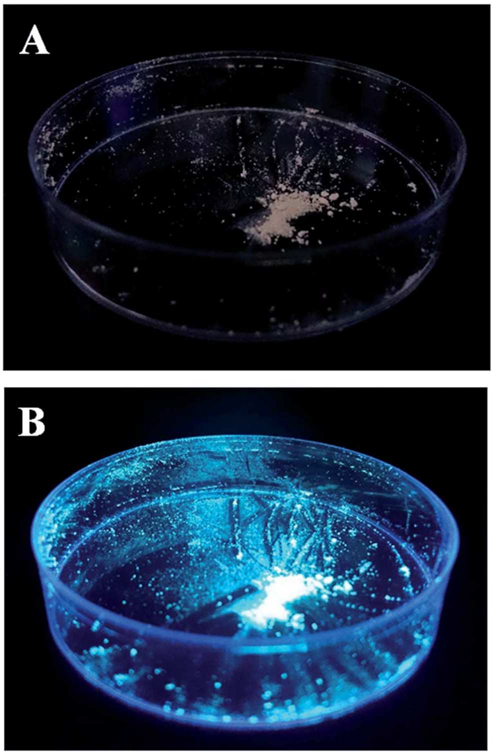


Fig. 3 Photographs of PVPy-grafted epoxy microspheres under: (A) incandescence and (B) ultraviolet ($\lambda = 365$ nm) illumination.

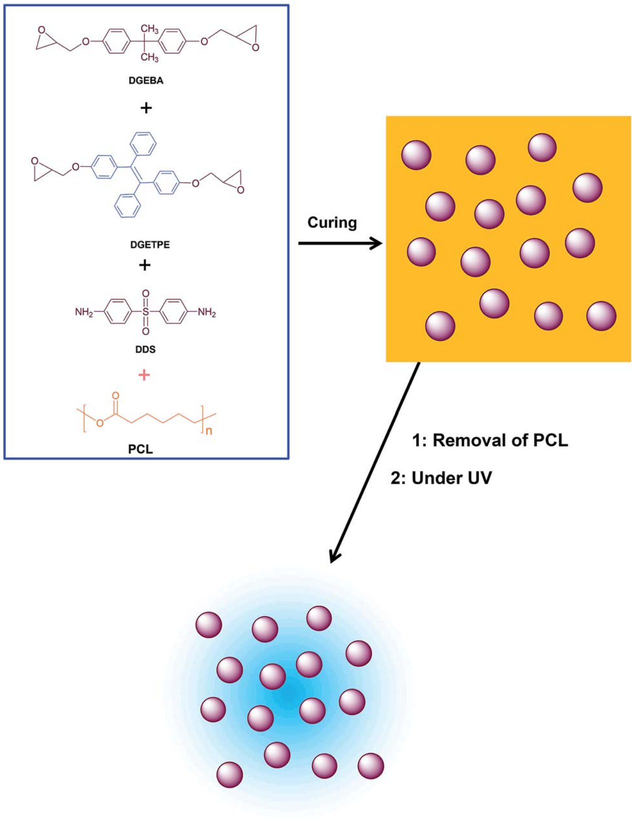
intense peak of resonance at 3.73 ppm disappeared whereas the peaks the range of 6.5–7.5 ppm remained unchanged. Concurrently, there appeared a minor peak at 4.64 ppm, which is assignable to the proton resonance of phenolic hydroxyl groups. The ^{1}H NMR spectroscopy indicates that the demethylation reaction has been performed to completion. With the occurrence of DHTPE with epichlorohydrin, there appeared several new signals of resonance at 2.63, 2.79, 3.22, 3.78 and 4.04 ppm, assignable to the protons of methylene and methine in glycidyl groups. According to the integral intensity of the methylene (or methine) protons to phenyl protons, it is judged that the all the phenolic hydroxyl groups of DHTPE were capped with glycidyl groups, *i.e.*, DGETPE was successfully obtained.

Preparation of epoxy microspheres

It has been reported that the reaction-induced phase separation occurred in the thermosetting blends of epoxy and poly(ε-caprolactone) (PCL) while 4,4′-diaminodiphenylsulfone (DDS) was used as the curing agent.[46,47] Notably, the phase inversion occurred while the content of PCL was 30 wt% or higher. The results of SEM showed that in the thermosetting blend, PCL was the continuous phase whereas epoxy was the dispersed phases in the form of spherical particles.[41] In this work, the thermosetting blend containing 30 wt% of PCL was thus utilized to prepare epoxy microspheres as descripted in Scheme 2. To obtain the luminescent epoxy microspheres, the mixture of DGETPE with DGEBA at the mass ratio of 1 : 9 was used as the epoxy monomer. Before the curing reaction, the mixture composed of DGEBA, DDS and PCL were homogenous transparent at the curing temperature (*viz.*, 150 °C). As the curing reaction proceeded, the initially transparent mixtures gradually became cloudy, indicating the occurrence of reaction-induced phase separation. After the continuous phase (*viz.* PCL) was removed *via* dissolution, the epoxy microspheres were thus obtained. The morphology of the as-obtained epoxy microspheres was examined by means of scanning electron microscopy (SEM) and the SEM micrographs were shown in Fig. 2. It is seen that the crosslinked epoxy microspheres with the size of 1–3 μm were successfully obtained. Fig. 3 shows the photographs of the epoxy microspheres under incandescence and ultraviolet ($\lambda = 365$ nm) illumination. Under incandescence, the epoxy microspheres were not luminescent (Fig. 3A). Under ultraviolet (λ = 365 nm), the materials emitted blue light (Fig. 3B). The above results indicate that the luminescent epoxy microspheres were successfully obtained.

Surface grafting polymerization *via* RAFT/MADIX process

The above epoxy microspheres were functionalized with a surface grafting-from methodology *via* reversible addition–fragmentation chain transfer/macromolecular design *via* the interchange of xanthate (RAFT/MADIX) approach as depicted in Scheme 3. First, the epoxy microspheres were subjected to a surface reaction with 2-bromopropionyl bromide to afford the modified epoxy microspheres, the surfaces of which bore 2-bromopropionyl groups. The result of the elemental analysis



Scheme 2 Preparation of luminescent epoxy microspheres *via* phase-inverted phase separation-induced polymerization.

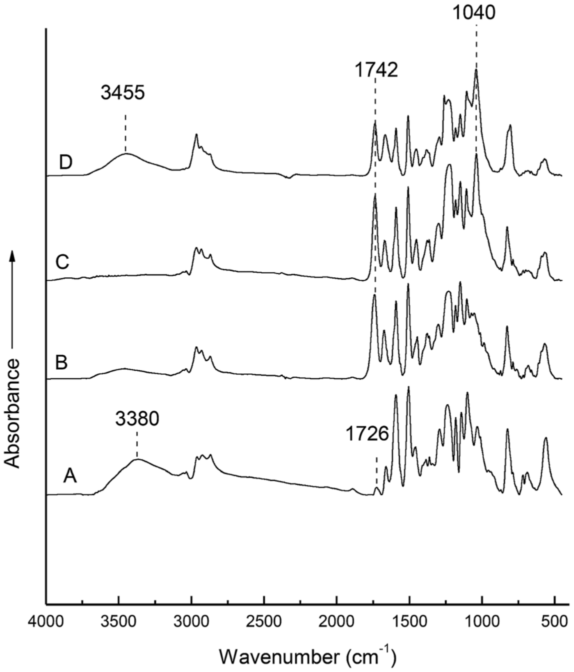
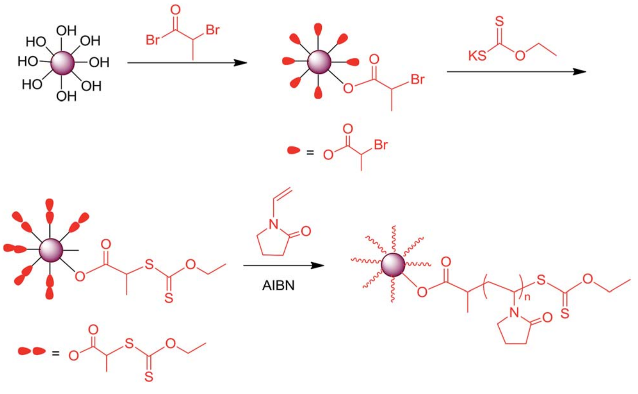


Fig. 4 FTIR spectra of: (A) unmodified, (B) 2-bromopropionyl-functionalized, (C) xanthate-functionalized, and (D) PVPy-grafted epoxy microspheres.

showed that the content of bromine was measured to be 1.4 mmol g^{-1}. These 2-bromopropionyl groups were allowed further to react with potassium ethyl xanthate to obtain the new epoxy microspheres, whose surfaces bore ethyl xanthate groups. The results of elemental analysis showed that the content of sulfur element was measured to be 3.76 mmol g^{-1}. Deducting the content of sulfur element in the curing agent (*viz.* DDS), the content of sulfur element in the form of ethyl xanthate groups at the surfaces of the epoxy microspheres were calculated to be 2.7 mmol g^{-1}. The ethyl xanthate groups could behave as the sites to grow the grafted polymer chains from the surfaces of the epoxy microspheres. In this work, the ethyl xanthate-functionalized epoxy microspheres were then used as the chain transfer agent to grow poly(*N*-vinyl pyrrolidone) (PVPy) chains *via* reversible addition–fragmentation chain transfer/macromolecular design *via* the interchange of xanthate (RAFT/MADIX) process. Shown in Fig. 4 are the FTIR spectra of the epoxy microspheres, the surface of which had different functional groups. For the control epoxy microspheres, the band at 3380 cm^{-1} is assignable to the stretching vibration of hydroxyl groups in hydroxyl ether structural units of amine-crosslinked epoxy. In addition, there appeared a minor band at 1726 cm^{-1}. This band is ascribed to the carbonyl groups of a small amount of PCL entrapped into the epoxy microspheres in the process of reaction-induced phase separation. Upon functionalization with 2-bromopropionyl bromide, there appeared a new band at 1742 cm^{-1}. This band is assignable to the stretching vibration of the carbonyl groups in the moiety of 2-bromopropionyl groups. The FTIR spectroscopy indicates that the surfaces of the epoxy microspheres were successfully functionalized with 2-bromopropionyl groups. Upon reacting with potassium ethyl xanthate, there appeared a new band at 1040 cm^{-1} compared to 2-bromopropionyl-functionalized epoxy microspheres. This band was assignable to the stretching vibrations of thiocarbonyl groups in the moiety of ethyl xanthate groups. The FTIR spectroscopy indicated that the surfaces of the epoxy microspheres were successfully functionalized with ethyl xanthate groups.

The epoxy microspheres bearing ethyl xanthate groups were used as the chain transfer agent for the RAFT polymerization of



Scheme 3 Surface functionalization of epoxy microspheres with a grafting-from polymerization methodology *via* a RAFT/MADIX process.

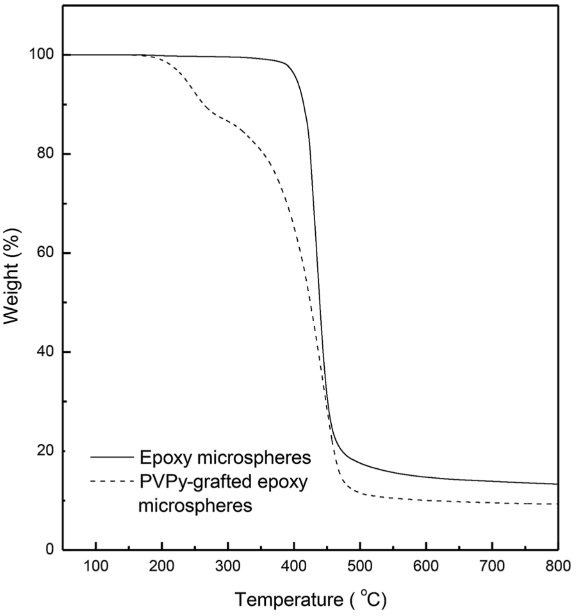


Fig. 5 TGA curves of the unmodified and PVPy-grafted epoxy microspheres.

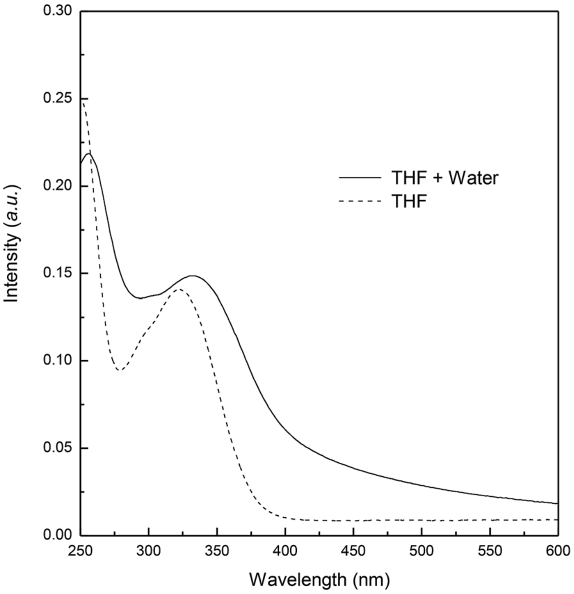


Fig. 6 UV absorption spectra of DGETPE in THF and the mixture of THF with water (THF : water = 1 : 99 vol).

N-vinyl pyrrolidone (NVP). With the polymerization, PVPy chains were grown from the surfaces of the epoxy microspheres, *i.e.*, the PVPy-grafted epoxy microspheres were obtained. The solubility test showed that the PVPy-grafted epoxy microspheres were easily dispersed in water, which was in marked contrast to the unmodified epoxy microsphere. This observation indicates that the water-soluble polymer (*viz.* PVPy) was successfully obtained. The morphology of the PVPy-grafted epoxy microspheres was investigated by means of scanning electron microscopy (SEM) and the SEM image is also presented in Fig. 2 (see Fig. 2B). For the unmodified epoxy microspheres, the surfaces were smooth; there was not the adhesion among the adjacent particles (see Fig. 2A). For the PVPy-grafted epoxy microspheres, the surfaces were coated with a layer of polymer (*viz.* PVPy) and some wrinkles were found at the surfaces of some particles. In addition, there was the adhesion among the adjacent particles (see Fig. 2B). These observations indicate that PVPy chains have been successfully grafted onto the surfaces of the epoxy microspheres. The control and PVPy-grafted epoxy microspheres were subjected to thermogravimetric analysis (TGA) and the TGA curves are shown in Fig. 5. The unmodified epoxy microspheres displayed one-step degradation profile and the initial degradation occurred at *ca.*, 400 °C. In contrast, the PVPy-grafted epoxy microspheres exhibited a two-step degradation profile at *ca.*, 236 and 400 °C, respectively. It is plausible to propose that the first one is attributable to PVPy chains which were grafted from the surfaces of the epoxy microspheres whereas the second to the epoxy. The results of FTIR, solubility test and TGA show that the PVPy-grafted epoxy microspheres were successfully obtained. In order to determine the mass fraction of the grafted PVPy chains, we further measured the content of the sulfur element by means of elemental analysis. The content of sulfur element at the ends of PVPy chains at the surfaces of the epoxy microspheres was measured to be 1.79 mmol g^{-1}. According to this value, the mass fraction of PVPy to epoxy was 33.8% in the PVPy-grafted epoxy microspheres.

Photophysical properties

Tetrahydrofuran (THF) was a good solvent of DGETPE whereas water is a non-solvent of DGETPE. Therefore, DGETPE would display an aggregation-induced emission phenomenon in the mixture of THF with water as a function of the concentration of water. The UV absorption and fluoresce spectra of DGETPE

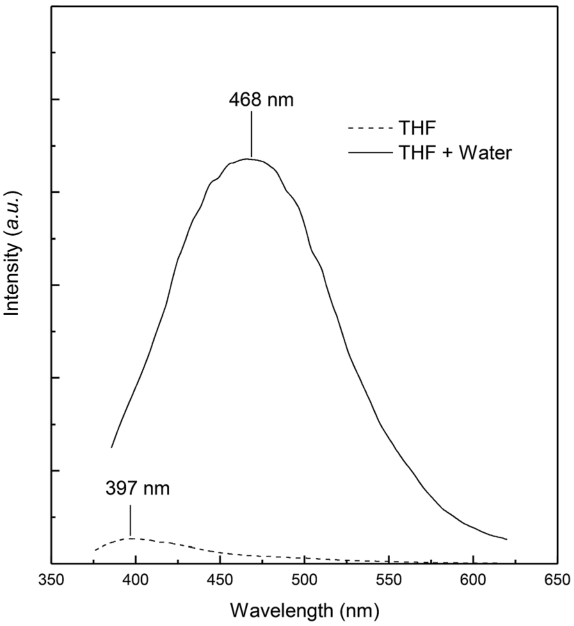


Fig. 7 FL spectra of DGETPE in THF and the mixture of THF with water (THF : water = 1 : 99 vol).

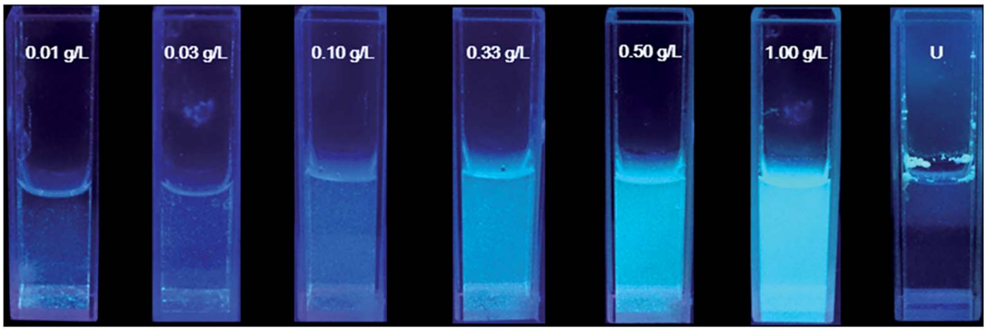


Fig. 8 Photographs of aqueous suspensions of unmodified and PVPy-grafted epoxy microspheres with various concentrations under ultraviolet illumination ($\lambda = 365$ nm).

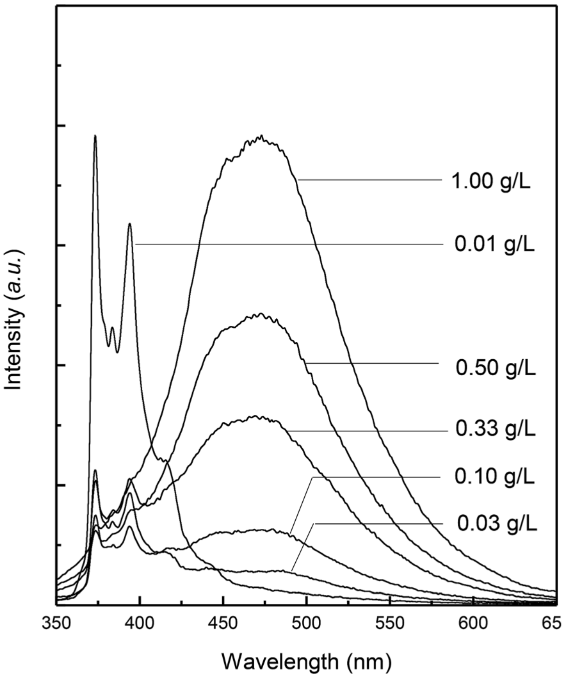


Fig. 9 FL spectra of PVPy-grafted epoxy microspheres with various concentrations at an excitation wavelength of $\lambda = 300$ nm.

dispersed in THF and its mixture of water (THF : water = 1 : 99 vol) are shown in Fig. 6 and 7. In the UV-vis absorption spectrum, DGETPE displayed an absorption band at $\lambda = 322$ nm in THF solution whereas the absorption occurred at $\lambda = 332$ nm in the mixture of THF with water. The bathochromic phenomenon reflected the change in conformation of the compound with the inclusion of water. In the THF solution, this compound displayed a feeble fluorescent emission band at *ca.* $\lambda = 397$ nm while it was excited with ultraviolet radiation of $\lambda = 330$ nm (see Fig. 7). Upon adding water to the THF solution at the concentration of 99 vol%, notably, a very strong fluorescent emission appeared at $\lambda = 468$ nm. This is a typical aggregation-induced emission (AIE) phenomenon. The increased intensity of fluorescent emission is attributable to the aggregation of DGETPE in the system owing to the incorporation of a large amount of non-solvent (*viz.*, water). For the fluorescent emission, notably, there was a red shift from 397 to 468 nm with the inclusion of a large amount of water. Owing to the inclusion of water, the rotation of aromatic ring in DGETPE was restricted in its aggregates, which facilitated the formation of the excimers.[48]

The above DGETPE was further incorporated into epoxy to prepare the luminescent epoxy microspheres *via* phase-inverted reaction-induced phase separation approach. It is expected that in the crosslinked network, the rotation of the aromatic rings of DGETPE would be restricted due to the constraint from the environmental crosslinked network. It is expected that the DGETPE moieties entrapped in the crosslinked network would convert photonic energy to emission, *i.e.*, a so-called crosslinking-induced emission occurred. To facilitate the dispersion of the epoxy microspheres in water, the surfaces of the microspheres were functionalized with PVPy, a water-soluble polymer. Shown in Fig. 8 are the photographs of the unmodified and PVPy-grafted epoxy microspheres dispersed in water at variable concentrations taken under UV illumination ($\lambda = 365$ nm). Notably, the epoxy microspheres were emissive in all the cases. The epoxy microspheres whose surfaces were not functionalized with PVPy floated above water in the form of aggregation. In marked contrast, the PVPy-grafted epoxy microspheres can well disperse in water; the intensity of the fluorescence increased with increasing the concentration of the microspheres in water. This observation indicates that the luminescent epoxy microspheres have been successfully functionalized with PVPy *via* surface grafting polymerization. The suspensions of the PVPy-grafted epoxy microspheres in water were further subjected to FL spectroscopy and the FL spectra are shown in Fig. 9. In all the cases, the PVPy-grafted epoxy microspheres displayed the intense emission. For the suspension with the concentration of 0.01 g L^{-1}, a few sharp bands were detected at $\lambda = 373$, 383, 394 and 415 nm, respectively. The separate FL bands could reflect the different restriction of intramolecular rotation (RIR) in TPE moiety entrapped in the environmental networks, *i.e.*, there existed the conformational anisotropy of TPE moiety. In the thermosetting polymer, the RIR process was activated owing to the formation of the crosslinked network, which exerted the constraint on the variation of the molecular conformation of TPE moiety. The TPE moieties in the crosslinked network were emissive owing to the environmental constraints although there is hardly the aggregation of the TPE moieties in the crosslinked network owing to the low ratio of DGETPE to DGEBA. This case is in marked contrast to the case that DGETPE was dissolved in THF (Fig. 7). The conformational anisotropy of TPE moieties in the crosslinked network gave rise to the polarized emission with different wavelengths. While the concentration of the PVPy-grafted epoxy microspheres was increased to 0.03 g L^{-1} or higher, the FL bands shifted to the position with a longer wavelength (*i.e.*, $\lambda = 469$ nm). The intensity of the bands increased with increasing the concentration of PVPy-grafted epoxy microspheres in the suspensions; in the meantime, the intensity of the bands in the range of 350–420 nm was significantly decreased. Generally, a bathochromic phenomenon of FL spectra with increasing the concentration of luminogen could be interpreted on the basis of: (i) the formation of excimer (and/or exciplex) and (ii) the light scattering effect of the epoxy microspheres. In the AIE systems, the restriction of intramolecular rotation (RIR) would be achieved *via* gathering of luminogens. The aggregation of luminogens would additionally promote the formation of excimers and thus the observed emission would result from the excimers with long wavelengths, *i.e.*, bathochromic phenomenon appeared.[49–53] In the present case, the aggregation of TPE moieties hardly occurred owing to the low concentration of DGETPE. The increase in the concentration of PVPy-grafted epoxy microspheres in the suspensions did not give rise to the aggregation of the luminogens. The bathochromic phenomenon could result from the light scattering of emissive light with the epoxy microspheres. The efficiency of the fluorescence process of the PVPy-grafted epoxy microspheres was examined by measuring the fluorescence quantum yield (Φ_F). In this work, Φ_F was measured with anthracene as the standard sample with its ethanol solutions with a series of concentrations. According to the refractive index values of the solvents, the Φ_F value was calculated to be 0.59%.

Conclusions

In this work, we successfully synthesized diglycidyl ether of tetraphenylethene (DGETPE), a novel epoxy monomer bearing a luminogen displaying AIE effect. With the thermosetting blends of epoxy with poly(ε-caprolactone), the DGETPE together with diglycidyl ether of bisphenol A (DGEBA) was used to prepare the epoxy microspheres *via* phase-inverted phase separation induced by reaction. The results of scanning electron microscopy (SEM) showed that the epoxy microspheres with the size of 1–3 μm in diameter were successfully obtained. The surfaces of the epoxy microspheres was modified with poly(*N*-vinyl pyrrolidone), a water-soluble polymers *via* surface grafting polymerization with RAFT/MADIX process. The PVPy-grafted epoxy microspheres can be well-dispersed into water. The epoxy microspheres are capable of emitting blue fluorescence under the irradiation of ultraviolet light. The luminescent behavior is attributable to the restriction of intramolecular rotation in DGETPE moieties with the formation of the crosslinked networks in the epoxy microspheres. The luminescent epoxy microspheres are potential in a variety of applications.

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